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Sunlight-catalyzed conversion of cyclic organics with novel mesoporous organosilicas

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Abstract

Porphyrin-embedded periodic mesoporous organosilica (PMO) materials were developed for sunlight-stimulated degradation of cyclic organics. The binding affinity and selectivity of the PMOs act to bring porphyrin and target into close proximity, provide extensive surface area, and a stable substrate for porphyrin immobilization. Aqueous samples incubated with these PMO materials showed a decrease in analyte concentration greater than that expected based on adsorption and uncatalyzed photoconversion during 5 h of sunlight illumination. Both materials show selective binding of TNT over structurally similar compounds such as *p*-nitrophenol. Template directed molecular imprinting was used in an attempt to increase the selectivity of the catalyst.

Keywords: Photocatalysis; Porphyrin; Molecular imprint; Mesoporous organosilica

1. Introduction

Periodic mesoporous organosilicas (PMOs) provide organic functionality in a silica matrix through the combination of covalently linked organic and silica components. Material characteristics can be tuned for a particular application by changing the organic groups used as ''bridges'' in the silica matrix [1]. The organic–inorganic polymers lend stability, selectivity, and ease of modification to applications traditionally protein- or microorganism-based. Template directed molecular imprinting, employing a target-like compound, can be used to alter pore homogeneity and distribution and to enhance selectivity and binding characteristics. The use of a regenerable diethylbenzene-bridged PMO for the preferential adsorption of hydrocarbons over time scales on the order of minutes has been demonstrated previously [2]. Other applications of PMOs include catalysis, filtration and/or purification, and chemical sensors [3–7].

A porphyrin is a nearly flat molecule with a macrocycle of four pyrrole rings joined by methine bridges. The porphyrin macrocycle binds cyclic compounds cofacially [8] even when the compound bears a nitrogen [9] or the porphyrin has a metal coordinated to the central nitrogen atoms [10]. They have been used as catalysts in a wide range of applications [11–14] including degradation of nitro-substituted toluene [11]. Porphyrins and metalloporphyrins are much less sensitive to variations in conditions such as temperature and pH than proteins and microorganisms withstanding temperatures above 150 °C [15]. The binding and catalytic characteristics of porphyrins can be altered through modification of the peripheral substituent groups or through incorporation of metals via coordination to the four central nitrogen atoms.

We have recently presented data that demonstrates the utility of combining the periodic mesoporous organosilica (PMO) with the porphyrin to achieve a semi-selective sensing element for the optical detection of cyclic organics [16]. We present data here that demonstrates the ability of these same materials to catalyze the conversion of nitroaromatics (Fig. 1) when placed under sunlight illumination.

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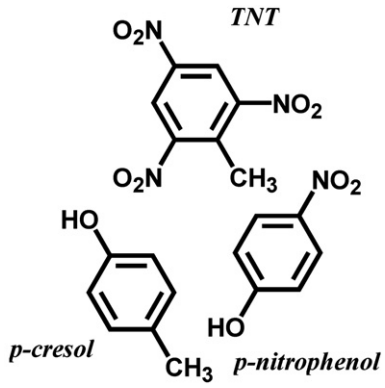

Fig. 1. The cyclic organic targets used in photocatalysis experiments.

2. Materials and methods

Meso-tetra(4-carboxyphenyl) porphine (CTPP) was obtained from Frontier Scientific, Logan, UT. 1,4-Bis(trimethoxysilylethyl)benzene was obtained from Gelest, Inc., Tullytown, PA. Brij®76, NaOH, HCl, ethanol, *p*-cresol, and *p*-nitrophenol were purchased from Aldrich, Milwaukee, WI. Pure re-crystallized TNT was obtained from the Naval Surface Warfare Center, Indianhead. The template molecule used to imprint the PMO material, decylamine trinitrobenzene (DATNB; Fig. 2), was synthesized in house [16].

The basic PMO preparation method used has been described in detail previously [2,17] (Fig. 2). For the non-imprinted material, Brij®76 was added to acidified water (20 g/L; ~2.4% HCl) while stirring. The mixture was covered and maintained at 50 °C for 12 h after which the precursor, 1,4-bis(trimethoxysilylethyl)benzene, was added and incubated 2 h further to obtain gelation. Synthesis of imprinted material followed a variation of this protocol in which the template, DATNB, was added after surfactant (Brij®76) equilibration. After 6 h of incubation at 50 °C, the solution was filtered using a 0.2 μm Teflon filter to remove excess template molecule. Further incubation over 3 h was followed by addition of precursor. For aging, drying, and surfactant removal, both imprinted and non-imprinted materials were handled identically [2]. For synthesis of the porphyrin-embedded materials (imprinted and non-imprinted), porphyrin was added simultaneously with the precursor material. Porphyrin-embedded materials were not refluxed in deionized water prior to surfactant removal. Physiochemical properties were characterized via gas sorption using nitrogen gas as the adsorbate at 77 K with a Micromeritics ASAP 2010 (Norcross, GA). For the porphyrin-embedded, *non-imprinted* PMO material (PMO-A) the BET surface area was 157 m^2/g with a total pore volume of 0.217 cm^3/g and pore size of 54 Å (BJH adsorption). For the porphyrin-embedded, imprinted material (PMO-B), the BET surface area was 144 m^2/g with a total pore volume of 0.221 cm^3/g and pore size of 54 Å (BJH adsorption) [16].

Samples of aromatic compounds were prepared as 10 ml aqueous solutions in Teflon capped glass test tubes at a concentration of 150 μM. Samples containing the analyte(s) under consideration and 10 mg of either PMO-A or PMO-B were placed on a rotary shaker outdoors in full sun (approx. 37 °C) for the time durations indicated. Analyte control solutions included identically prepared solutions at 150 μM with no PMO material which were either

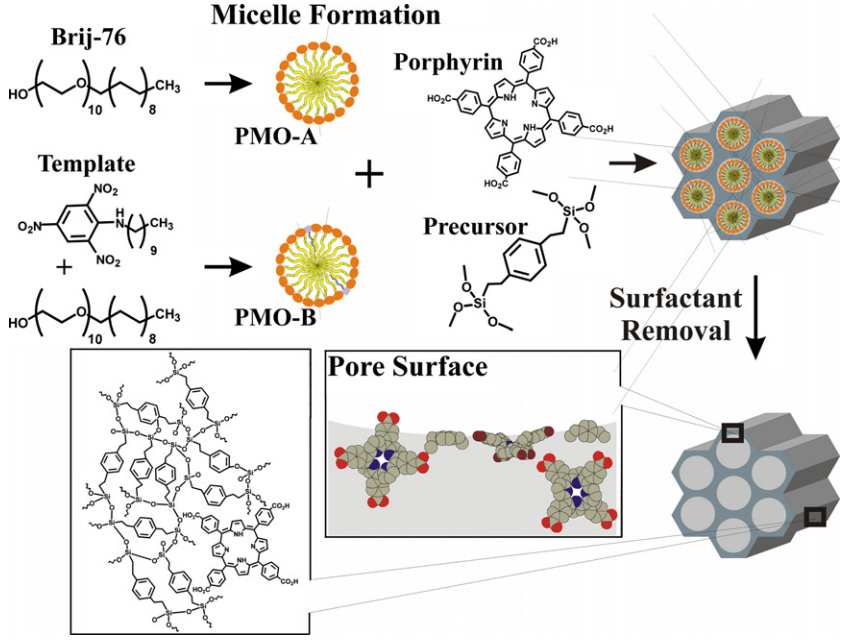

Fig. 2. Synthesis and molecular structures [17]. Synthesis of the PMOs begins with micelle formation. In the case of PMO-A micelles consist of Brij-76 only while PMO-B uses a mixture of Brij-76 and the template molecule. The PMO materials consist of amorphous precursor and porphyrin. The material pore surfaces vary in that imprinting of PMO-B against a target-like molecule provides a higher number of sites that are favorable to the binding of TNT.

exposed to sunlight or protected from sunlight. Prepared analyte solutions containing one of the PMO materials were also used as dark control samples. Control solutions were exposed to temperature and handling procedures identical to those experienced by the samples. Solutions not exposed to sunlight were protected with aluminum foil wrapper. Immediately following the incubation period, samples were filtered using 0.2 μm PTFE Acrodisc syringe filters (Gelman Sciences, Ann Arbor, MI).

Concentrations of the solutions used were measured by HPLC using EPA method 8330 on a Waters HPLC system with dual 510 pumps and a 717 autosampler coupled to a photodiode array detector. A 250 mm Altech Altima C18 column was employed with an isocratic 50:50 methanol:water mobile phase. Difference method was used to determine changes in concentration. Absorbance spectra were collected in 96-well format using a Tecan XSafire monochromator-based microplate reader from 285 to 800 nm with 3 nm resolution. Fitting of data was accomplished in PSI-Plot (v7.5, Polysoftware, Int.) to a 98% confidence interval.

3. Results

Homogenous analyte solutions were used to determine baseline levels for changes in concentration under the experimental conditions. Aqueous analyte solutions prepared at 150 μM that were protected from sunlight showed no change in concentration over a 5 h incubation period. Incubation of identical samples in sunlight showed a linear decrease in concentration over the 5 h incubation period (Fig. 3). For *p*-cresol (pCR) and *p*-nitrophenol (pNP), the total change in concentration was minimal compared to the initial sample concentration. In the case of TNT, 32% of the original concentration remained after 5 h sunlight exposure (Fig. 3). Nearly identical changes in concentration are observed when a ternary mixture containing pCR, pNP, and TNT (each analyte at 150 μM) is incubated in sunlight.

The adsorption of the analytes under consideration by each of the porphyrin-embedded PMO materials was investigated to obtain baseline values for concentration changes in the analyte solutions. When 10 mg of PMO material (either A or B) was placed in a 150 μM aqueous solution of analyte at 37 °C, pNP and pCr adsorption reached equilibrium in less than 30 mins while that of TNT reached equilibrium after about 1 h. Adsorption values are reported in Table 1 for samples incubated over a period of 5 h. The PMO-B material showed approximately 20% less total adsorption for the three analytes than PMO-A when analytes were presented as single component solutions. TNT adsorption was not impacted by the presence of pNP and pCr in solution for either PMO material. For the non-imprinted PMO-A, a 20% reduction in adsorption of both pNP and pCr was observed in the ternary mixture. PMO-B showed a similar reduction in adsorption of pCr with a 35% reduction in pNP adsorption.

Table 1
Adsorption of analytes by PMO materials

	Analyte	PMO-A		PMO-B	
		μmol/g	nmol/m^2	μmol/g	nmol/m^2
Single analyte	TNT	127	809	102	708
	pCr	47	299	35	243
	pNP	34	217	28	194
Ternary mixture	TNT	124	790	108	750
	pCr	39	248	29	201
	pNP	28	178	18	125

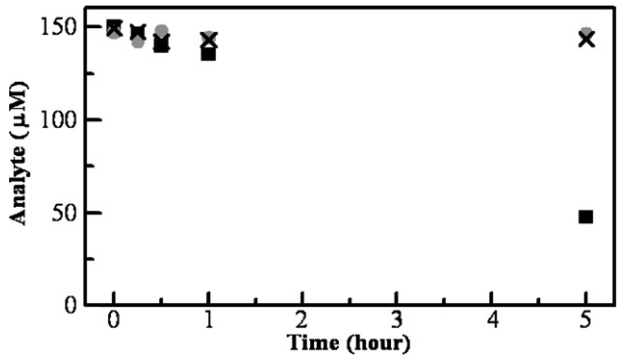

Fig. 3. Single analyte aqueous solutions of *p*-cresol (●), *p*-nitrophenol (×), and 2,4,6-trinitrotoluene (■) at 150 μM incubated over a 5 h period under sunlight illumination in the absence of PMO materials.

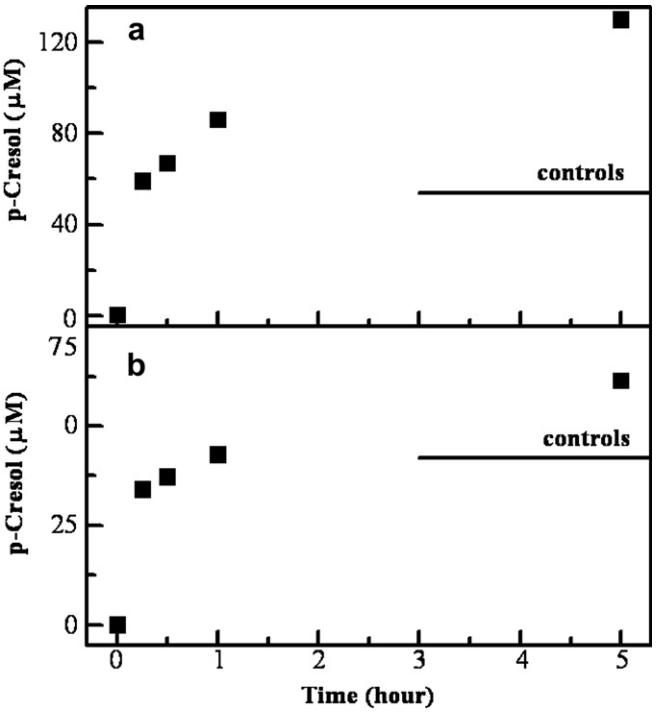

Fig. 4. *p*-Cresol removed from solution as a function of time when incubated with either PMO-A (a) or PMO-B (b) under sunlight illumination. Solid lines show the sum of the total change in concentration after 5 h due to analyte adsorbed under dark conditions and sunlight illumination in the absence of PMO materials.

Table 2
Change in analyte content (nmol) of single and ternary analyte aqueous samples after 1 and 5 h incubation

	Condition	PMO-A			PMO-B		
		pNP	pCr	TNT	pNP	pCr	TNT
Single analyte samples							
Change after 1 h	Control	404	517	1350	349	411	1210
	Illuminated	480	888	1440	450	456	1390
Change after 5 h	Control	410	528	2290	350	408	2140
	Illuminated	748	1330	1500	688	642	1490
Ternary analyte mixtures							
Change after 1 h	Control	344	407	1320	248	305	1190
	Illuminated	442	391	1360	370	359	1270
Change after 5 h	Control	348	438	1260	252	346	2102
	Illuminated	705	499	1480	541	353	1477

Control value is the sum of changes from incubation of analyte(s) alone with sunlight illumination and adsorption by the PMO; illuminated value is the change upon incubation of analyte and PMO with sunlight illumination.

Illumination of single analyte solutions containing 150 μM pNP, pCr, or TNT and 10 mg of either PMO-A or PMO-B showed rates of change in concentration greater than that expected for the sum of uncatalyzed sunlight degradation of the analytes and adsorption onto the PMO material. Fig. 4 shows the results of incubation of pCr with the two materials under sunlight illumination. After 1 h of incubation in sunlight with PMO-A, 888 nmol of pCr had been removed from the solution. This was well in excess of the total expected due to adsorption and uncatalyzed sunlight degradation in the absence of catalyst, 517 nmol. Though adsorption was expected to reach equilibrium after less than 1 h, the concentration of pCr in solution continued to change throughout the 5 h incubation (Fig. 4). Similarly, incubation under sunlight illumination increased the change in concentration for pNP when in the presence of either PMO-A or PMO-B as either single analyte or ternary solutions. Table 2 summarizes the increase in analyte removed from solution by the PMO materials as a result of sunlight exposure.

4. Discussion

The potential of two porphyrin-embedded periodic mesoporous organosilica materials to catalyze sunlight driven degradation of cyclic organics in aqueous solution was investigated and the impact of template directed molecular imprinting on TNT selectivity was analyzed. The change in concentration of the analytes pNP and pCr upon incubation with the PMO materials under sunlight illumination exceeded that expected based on the uncatalyzed photoconversion and adsorption values. This indicates the involvement of the PMO materials in a sunlight stimulated reaction. While the pNP and pCr losses clearly illustrate the effectiveness of the porphyrin-embedded material to enhance the sunlight driven degradation of the compounds, the TNT results are less than convincing. This is likely attributable to the higher affinity of the PMO materials for this analyte and the relatively high uncatalyzed photoconversion rate. Experiments were also conducted using ternary mixtures of the analytes (Table 2) though analysis is complicated by strong TNT adsorption and fast solution photoconversion. The conversion of pCr is dramatically reduced for both PMO materials when analytes are presented as mixtures while pNP conversion is impacted only for PMO-B. Improved selectivity of the materials upon imprinting would explain this difference though the experiment does not exclude other possibilities.

Though TNT samples are initially clear, a pink color develops quickly upon exposure to sunlight in aqueous solution. This rapid conversion of TNT in the presence of sunlight and water makes the changes in concentration upon incubation with the PMO materials difficult to analyze. If end-point analysis is used after 5 h incubation, the results are inconclusive with changes in the TNT concentration attributable to only uncatalyzed photoconversion and adsorption by the PMO materials. Even at the 1 h time point, the advantage of incubation with the PMO materials under sunlight illumination is arguable. The pink color observed to develop in the TNT samples is attributable to 1,3,5-trinitrobenzene (TNB), a product of TNT photoconversion. For the HPLC method employed, TNB is eluted with the void volume of the sample making quantification of its presence impossible. In order to attempt to address this difficulty, absorbance values for the samples at 435 nm were measured. Based on these absorbance values, the TNB concentration for samples increases more rapidly than that of control samples containing no PMO when both are illuminated by sunlight. This data indicates the potential involvement of the PMO in enhancement of sunlight catalyzed degradation of TNT. The final concentration of TNB in the PMO-B containing samples after illumination (based on 435 nm absorbance) is 37% less than that of illuminated samples containing TNT and no PMO (data not shown), however, drawing conclusions based on this information is difficult due to the likely adsorption of TNB onto the PMO materials.

The two PMO materials vary in that the synthesis of PMO-B involved the use of template directed molecular imprinting (TDMI) against decylaminetrinitrobenzene, a

TNT analog. TDMI should tend to generate sites on the pore surface that are more specific to TNT binding by providing sites that are complimentary to the TNT molecule. Parameters affected by imprinting may include van der Waals force, induction forces, electrostatic interactions, and even steric considerations. For example, sites on the pore surface providing TNT-specific multipole interactions and hydrogen bonding will not necessarily be optimized for interactions with pNP [18]. Though a small improvement in selectivity (noted as a decrease in pNP adsorption from the ternary mixture for PMO-B) was obtained, it was at the expense of total adsorption of the target, TNT. Experiments using a mixture of analytes demonstrate that both of these less than optimal materials still achieve some degree of selectivity for TNT over pNP and pCr. As seen in Table 1, the adsorption of TNT is unaffected by the presence of pCr and pNP in solution.

When compared to previously synthesized PMO materials, the porphyrin-embedded materials have reduced specific surface area. The presence of porphyrin in the materials likely disrupts the normal PMO structure to some extent. Porphyrin-free versions of the two PMOs synthesized using the methods described have achieved BET surface areas from 400 to 500 m^2/g and total pore volumes of 0.4–0.5 cm^3/g as compared to 150 m^2/g and 0.2 cm^3/g obtained here for the porphyrin-embedded versions. Optimization of these materials is ongoing. Several methods of incorporation of the porphyrin into the PMO materials are being investigated as are variations of the template directed molecular imprinting process.

Though these materials are in the early stages of development, the results presented here demonstrate the potential for the development of effective photocatalysts through the combination of porphyrins with periodic mesoporous organosilicas. The porphyrin bound to the PMO materials is stabilized against the photo-degradation observed when it is sunlight illuminated in solution (data not shown). The PMOs used here were optimized for adsorption of TNT and similar compounds, however, PMO materials can be synthesized for adsorption of chemical warfare agents, pesticides, volatile organic compounds, or toxic industrial products to name a few. It should be possible to engineer a material or family of materials so that undesirable by-products of the catalyzed reaction could be re-adsorbed onto other sites in the material and further converted with the ultimate goal being to produce products that can be safely released into the environment. Potential applications include situations such as inline water treatment, environmental clean up, and exhaust stack filtering.

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